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Blue Photoluminescence N-Substituted Poly(4*H*-benzo[*def*]carbazole)s

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Abstract: N-Alkyl and N-phenyl substituted poly(carbazole)s having a 4,5-ethenylene bridge, poly(4*H*-benzo[*def*]carbazole)s, were newly synthesized. Poly(carbazole)s having a 4,5-ethylene bridge were also synthesized for comparison. They were prepared from corresponding dibromo monomers by Ni(0)-catalyzed Yamamoto polycondensation. All the polymers had good solubility in common organic solvents, enough high molecular weights to make thin films, and good thermal stability showing about 400 °C of temperature at 5 wt% loss in TGA. The band gaps of these polymers were in the range of 2.77-3.15 eV which were appropriate for bluish light emissions. The absorption and emission maxima of these polymers in CHCl₃ were in the ranges of 361-396 and 419-456 nm, respectively. These polymers showed good fluorescence quantum efficiencies in CHCl₃. The energy levels of highest occupied molecular orbital of the poly(benzocarbazole)s were shallower than those of corresponding 4,5-ethylene bridged poly(carbazole)s.

Keywords: Conjugated polymer, Carbazole, Photoluminescence

1. Introduction

The polymeric light-emitting diodes (PLEDs) have been investigated to be practically used as display devices, because they can be fabricated with simple coating techniques and show tolerable emitting efficiencies. [1]. Among three basic colors of blue, green, and red for full-color displays, development of high-efficiency blue-light-emitting materials is important. Because the short-wavelength emission can serve as an excitation source for emissions over the whole visible range [2]. Since the first report on blue PLEDs device which was fabricated with poly(*p*-phenylene) (PPP) in 1992 [3], a large number of materials for blue-light-emitting have been developed [4-8]. Among the blue-light-emitting polymers, fluorene-based conjugated polymers have been recognized as a promising class, because they are good processable materials and show rarely high

fluorescent performances in the solid state [9, 10]. Unfortunately, polyfluorene-based PLEDs have usually emitted impure blue colors due to emissions from contaminants such as excimers and keto-defects in addition to principal emission from β -phase [11]. Since early in this century, poly(2,7-carbazole)s regarded as a strained planner poly(4,4'-biphenylene) with an imino-bridge have been considered as a new candidate for blue light emitting materials comparable to the fluorene-based polymers, because they have wide band gaps appropriate for blue light emissions, sharp emission bands in the solid film state, and smaller ionization potentials compared to polyfluorenes [12-16].

In this paper, several new poly(carbazole)s for stable light emitting are attempted to synthesize by bridging a carbazole (**Cz**) unit with 4,5-ethynylene to construct the benzo[*def*]carbazole (**BCz**) structure as shown in Fig. 1. Dehalogenative polycondensation of 2,6-dibrominated and 1,7-dibrominated **BCz** monomers gave corresponding poly(benzo[*def*]carbazole)s (**PBCz**). In parallel, 4,5-ethylene bridged polycarbazoles, poly(8,9-dihydro-2,6-benzo[*def*] carbazole)s (**PECz**), were also synthesized from the precursor derivatives of the ethylene bridged carbazoles (**ECz**) for comparison. Basic properties of these polymers were compared with those of poly(2,7-carbazole)s and poly(3,6-carbazole)s.

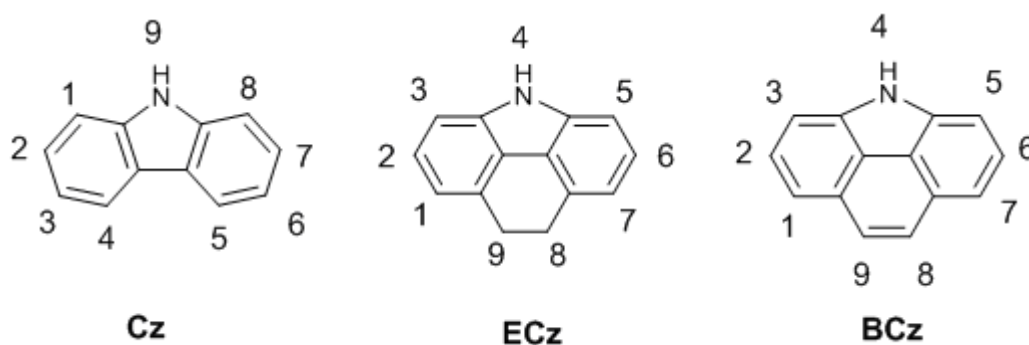
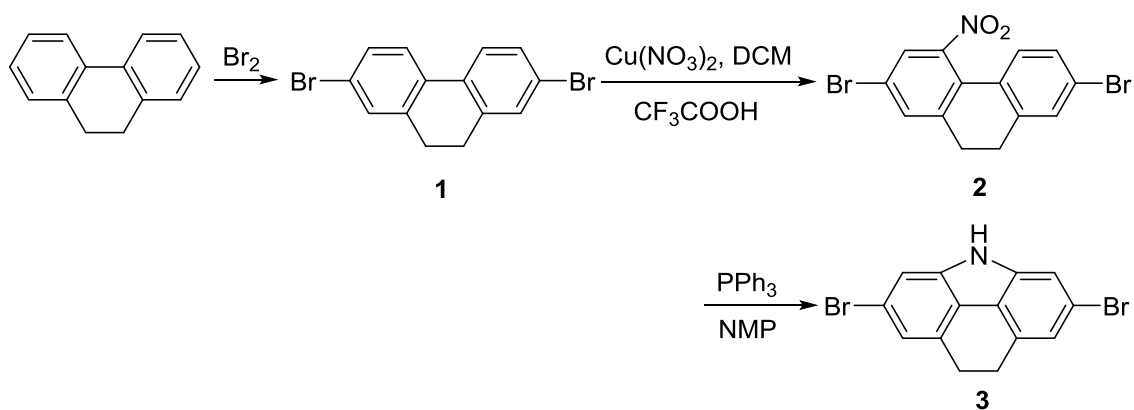


Fig. 1 The structures and numbering system of **Cz**, **ECz** and **BCz**

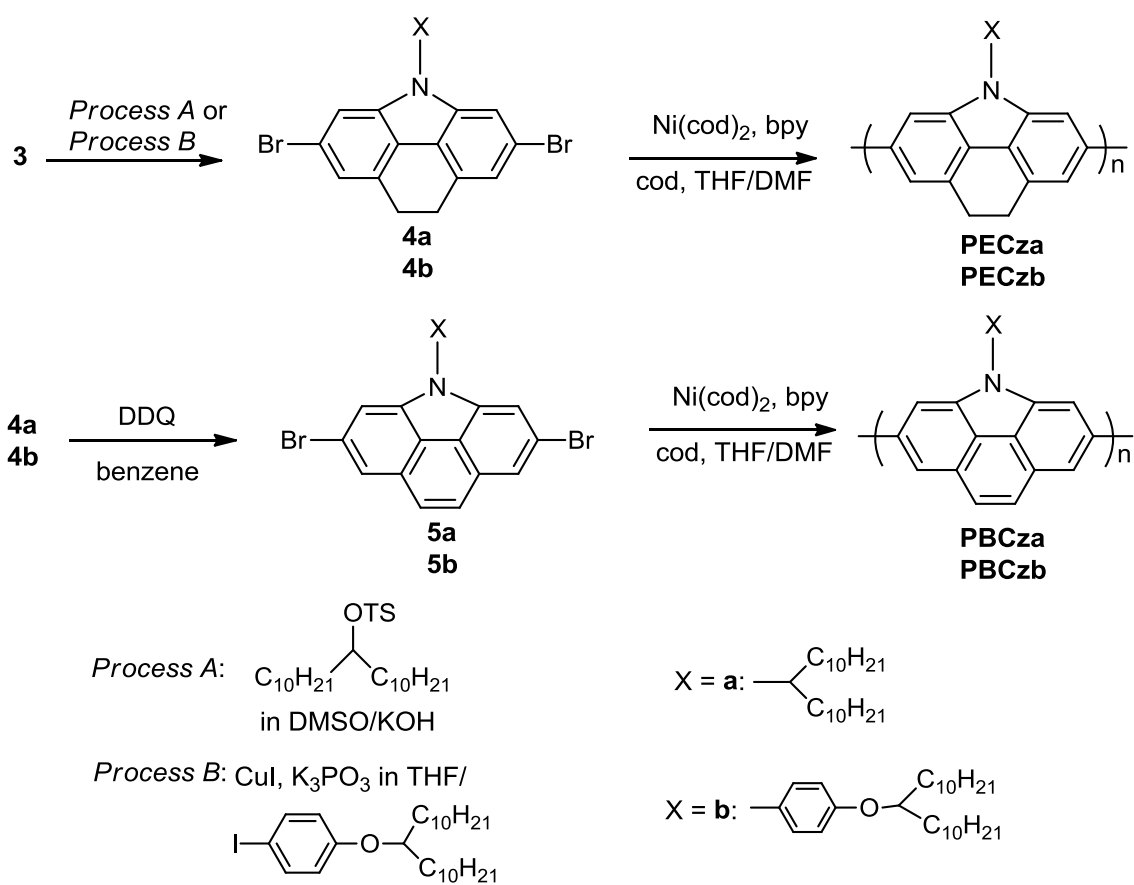
2. Experimental

2.1 Materials

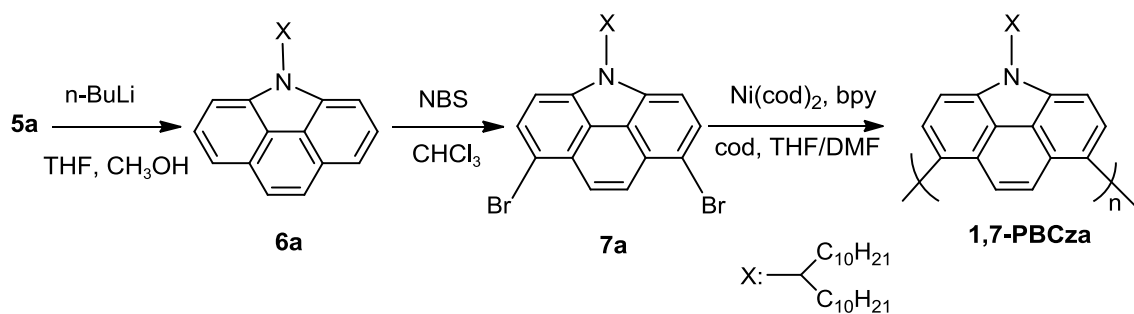
1-Decylundecyl-4-methylbenzenesulfonate and 1-(1-decylundecyloxy)-4-iodobenzene were synthesized according to the procedures reported previously [17, 18]. 2,6-Dibrominated **ECz** (**3**) was synthesized by reductive ring closure of **2** that was prepared by nitration of **1** according to the procedures reported previously (Scheme 1 see Supporting information) [19]. Reagents and solvents were purchased from Kanto Chemical, Tokyo Chemical Industry, Aldrich and Nacalai Tesque Inc. Dimethylformamide (DMF) and benzene distilled after drying with CaH_2 were stored under an argon atmosphere. Tetrahydrofuran (THF) distilled after drying with sodium was stored under an argon atmosphere. The other solvents and all commercially available reagents were used without further purification.



Scheme 1. Synthetic route of 2,6-dibromo-8,9-dihydrobenzo[def] carbazole



Scheme 2. Synthetic routes of **PECz** and **PBCz**



Scheme 3. Synthetic route of **1,7-PBCza**

2,6-Dibromo-N-(1-decylundecyl)-8,9-dihydrobenzo[def]carbazole (4a). To suspension of **3** (2 g, 5.7 mmol) and potassium hydroxide (1.46 g, 26 mmol) in dimethyl sulfoxide (DMSO) (25 mL) was added dropwise solution of 1-decylundecyl-4-methylbenzenesulfonate (2.65 g, 5.7 mmol) in DMSO (14 mL) under argon. The mixture was stirred at room temperature for 6 h. Then the mixture was poured into water. After extraction with dichloromethane, drying over MgSO_4 and evaporation of the solvent, the crude product was purified by column chromatography (silica gel, dichloromethane/hexane, 1:1, as an eluent), giving yellow oil (2.27 g, 62%). ^1H NMR (400 MHz, CDCl_3) δ [ppm]: 7.34 (s, 2H), 7.11 (s, 2H), 4.24 (m, 1H), 3.28 (s, 4H), 2.13-2.09 (m, 2H), 1.89-1.85 (m, 2H), 1.28-1.14 (m, 32H), 0.88-0.84 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ [ppm]: 138.6, 131.4, 120.8, 119.9, 120.0, 111.4, 57.6, 34.0, 31.8, 29.6, 29.5, 29.4, 29.3, 29.2, 26.1, 22.6, 14.1. Calcd for $\text{C}_{35}\text{H}_{51}\text{Br}_2\text{N}$ (645.61): C, 65.11; H, 7.96; N, 2.17. Found: C, 65.42; H, 8.21; N, 2.20.

2,6-Dibromo-N-(p-(1-decylundecyloxy)phenyl)-8,9-dihydrobenzo[def]carbazole (4b). Suspension of potassium phosphate (0.8 g, 3.7 mmol), **3** (0.66 g, 1.9 mmol), CuI (3.6 mg, 1.9 mmol), 1-(1-decylundecyloxy)-4-iodobenzene (4.37 g, 8.5 mmol) and trans-1,2-cyclohexanediamine (0.011 mL, 0.094 mmol) in THF (3 mL) was stirred at 65 °C for 3 days. After cooling to room temperature, the mixture was poured into water. After extraction with dichloromethane, drying over MgSO_4 and evaporation of the solvent, the crude product was purified by column chromatography (silica gel, hexane as an eluent) to give a white solid (1.1 g, 60%). ^1H NMR (400 MHz, CDCl_3) δ [ppm]: 7.43 (d, $J = 6.8$ Hz 2H), 7.39 (s, 2H), 7.18 (s, 2H), 7.06 (d, $J = 8.0$ Hz 2H), 4.28 (m, 1H), 3.32 (s, 4H), 1.73-1.67 (m, 4H), 1.43-1.27 (m, 32H), 0.90-0.86 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ [ppm]: 157.7, 139.0, 131.3, 130.0, 126.1, 126.0, 121.2, 121.1, 120.5, 116.9, 111.2, 78.5, 33.9, 31.9, 31.5, 29.7, 29.6, 29.3, 26.1, 25.4, 22.7, 22.6, 14.1. Calcd for $\text{C}_{41}\text{H}_{55}\text{Br}_2\text{NO}$ (737.71): C, 66.65; H, 7.52; N, 1.90. Found: C, 66.31; H, 7.68; N, 1.97.

2,6-Dibromo-4-(1-decylundecyl)-4H-benzo[def]carbazole (5a). A mixture of **4a** (0.5 g, 0.78 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.42 g, 1.8 mmol) in benzene (77 mL) was refluxed for 8 h under a N_2 atmosphere. After cooling to room temperature, the mixture was poured into water. After extraction with dichloromethane, drying over MgSO_4 and evaporation of the solvent, the crude product was purified by column chromatography (silica gel, hexane as an eluent) to give a white solid (0.42 g, 85%). ^1H NMR (400 MHz, CDCl_3) δ [ppm]: 7.96 (s, 2H), 7.90 (s, 2H), 7.66 (s, 2H), 4.52 (m, 1H), 2.29-2.25 (m, 2H), 2.01-1.95 (m, 2H), 1.25-1.11 (m, 32H), 0.89-0.83 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ [ppm]: 138.1, 127.7, 126.0, 120.7, 118.3, 118.2, 110.0, 58.1, 34.3, 31.9, 29.7, 29.6, 29.5, 29.4, 29.2, 25.3, 22.6, 14.1. Calcd for $\text{C}_{35}\text{H}_{49}\text{Br}_2\text{N}$ (643.59): C, 65.32; H,

7.67; N, 2.18. Found: C, 65.57; H, 8.02; N, 2.05.

2,6-Dibromo-4-(p-(1-decylundecyloxy)phenyl)-4H-benzo[def]carbazole (5b). Dibromobenzo-carbazole **5b** was similarly synthesized according to the procedure for **5a**, giving yellow oil (0.48 g, 96%). ¹H NMR (400 MHz, CDCl₃) δ [ppm]: 7.99 (s, 2H), 7.96 (s, 2H), 7.75 (s, 2H), 7.62 (d, J= 9.1 Hz 2H), 7.14 (d, J= 9.1 Hz 2H), 4.32 (m, 1H), 1.73-1.69 (m, 4H), 1.33-1.27 (m, 32H), 0.90-0.85 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ [ppm]: 157.8, 140.8, 130.3, 127.8, 126.2, 126.0, 121.2, 120.1, 119.3, 117.0, 109.9, 78.6, 33.9, 31.9, 31.5, 29.7, 29.6, 29.3, 25.4, 22.7, 22.6, 14.1. Calcd for C₄₁H₅₃Br₂NO (735.69): C, 66.84; H, 7.26; N, 1.90. Found: C, 66.47; H, 7.50; N, 1.75.

4-(1-Decylundecyl)-4H-benzo[def]carbazole (6a). Dibromobenzocarbazole **5a** (0.8 g, 1.24 mmol) was dissolved in 12.5 mL of anhydrous THF and cooled to -78 °C under nitrogen atmosphere, in which 1.6 M n-BuLi/hexane solution (1.63 mL, 2.6 mmol) was added dropwise with stirring. The mixture was kept at -78 °C for 20 min and then 0.4 mL of methanol was added. The reaction mixture was stirred at room temperature for 1 h, quenched with 40 mL of water, and extracted with dichloromethane. After drying over MgSO₄ and the solvent evaporation, the crude product was purified by column chromatography (silica gel, hexane as an eluent) to give a white solid (0.428g, 72%). ¹H NMR (400 MHz, CDCl₃) δ [ppm]: 8.05 (s, 2H), 7.81(t, J= 7.8 Hz 2H), 7.73 (d, J= 7.3 Hz 2H), 7.54 (d, J= 7.8 Hz 2H), 4.66 (m, 1H), 2.38-2.35 (m, 2H), 2.02-1.99 (m, 2H), 1.24-1.09 (m, 32H), 0.90-0.82 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ [ppm]: 129.4, 127.4, 126.5, 126.0, 121.6, 115.9, 114.5, 57.6, 34.5, 31.9, 31.8, 29.7, 29.6, 29.4, 29.3, 25.4, 22.6, 14.1.

1,7-Dibromo-4-(1-decylundecyl)-4H-benzo[def]carbazole (7a). A mixture of **6a** (0.35g, 0.72 mmol) and NBS (0.26g, 1.44 mmol) in CHCl₃ (3.5 mL) was stirred at 40 °C for 8 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was poured into water. After extraction with dichloromethane, drying over MgSO₄ and evaporation of the solvent, the crude product was purified by column chromatography (silica gel, hexane as an eluent) to give a white solid (0.327g, 70%). ¹H NMR (400 MHz, CDCl₃) δ [ppm]: 8.17 (s, 2H), 7.97 (d, J= 7.7 Hz 2H), 7.43 (d, J= 7.8 Hz 2H), 4.59 (m, 1H), 2.33-2.17 (m, 2H), 1.98-1.95 (m, 2H), 1.25-1.08 (m, 32H), 0.88-0.82(m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ [ppm]: 140.1, 133.8, 129.9, 127.6, 126.1, 108.4, 57.9, 34.4, 31.8, 31.6, 29.6, 29.4, 29.3, 29.2, 26.0, 22.6, 14.1.

Poly[8,9-dihydro-N-(1-decylundecyl)-4H-benzo[def]carbazole-2,6-ylene] (PECza). Under an argon atmosphere, a solution of bis(1,5-cyclooctadiene)nickel(0) (Ni(cod)₂) (0.28 g, 1.03 mmol), 2,2'-bipyridine (bpy) (0.18 g, 1.15mmol) and 1,5-cyclooctadiene (cod) (0.25 g, 2.38 mmol) in DMF (2.5 mL) was heated to 80 °C for 30 min. The **4a** (0.301 g, 0.46 mmol) dissolved in THF (2.5 mL) under argon was added to the DMF solution. The reaction solution was heated at 80 °C for 3 days. After the reaction solution was cooled to room temperature, the resultant polymer was precipitated from methanol/HCl aq, and reprecipitated from methanol/NH₃ aq and from methanol, respectively. The precipitate was successively extracted with acetone, hexane and CHCl₃ by Soxhlet extraction. The CHCl₃ extract was again precipitated from methanol. **PECza** was obtained as a yellow soild (0.21 g, 92%). ¹H NMR (400 MHz, CDCl₃) δ [ppm]: 7.48 (s, 2H), 7.32 (s, 2H), 4.56-4.54 (m, 1H), 3.50 (s, 4H), 2.36 (m, 2H), 1.99-1.96 (m, 2H), 1.32-1.23 (m, 32H), 0.90-0.82 (m, 6H). Calcd for C₃₅H₅₃N (487.82): C, 86.18; H, 10.95; N, 2.87. Found: C, 86.25; H, 10.24; N, 2.95.

Poly[8,9-dihydro-N-(p-(1-decylundecyloxy)phenyl)-4H-benzo[def]carbazole-2,6-ylene] (**PECzb**). In a similar way to the synthetic procedure for **PECza**, polymerization of **4b** gave **PECzb** as a yellow solid (0.22 g, 94%). ¹H NMR (400 MHz, CDCl₃) δ [ppm]: 7.63 (d, J = 8.4 Hz 2H), 7.51 (s, 2H), 7.32 (s, 2H), 7.08 (d, J = 8.4 Hz 2H), 4.27 (m, 1H), 3.47 (s, 4H), 1.70-1.66 (m, 4H), 1.30-1.24 (m, 32H), 0.90-0.83 (m, 6H). Calcd for C₄₁H₅₇NO (645.61): C, 84.92; H, 9.91; N 2.42. Found: C, 84.95; H, 9.32; N, 2.56.

Poly[4-(1-decylundecyl)-4H-benzo[def]carbazole-2,6-ylene] (**PBCza**). Similarly, polymerization of **5a** gave **PBCza** as a yellow solid (0.16 g, 91%). ¹H NMR (400 MHz, CDCl₃) δ [ppm]: 8.25 (s, 2H), 8.20 (s, 2H), 8.03 (s, 2H), 4.90(m, 1H), 2.60 (m, 2H), 2.18 (m, 2H), 1.41-1.17 (m, 32H), 0.90-0.78 (m, 6H). Calcd for C₃₅H₅₁N (485.80): C, 86.53; H, 10.28; N, 2.88. Found: C, 86.35; H, 10.28; N, 2.81.

Poly[4-(p-(1-decylundecyloxy)phenyl)-4H-benzo[def]carbazole-2,6-ylene] (**PBCzb**). Similarly, polymerization of **5b** gave **PBCzb** as a yellow solid (1.1 g, 65%). ¹H NMR (400 MHz, CDCl₃) δ [ppm]: 8.21 (s, 4H), 8.08 (s, 2H), 7.87 (d, J = 7.6 Hz 2H), 7.18 (d, J = 8 Hz 2H), 4.32 (m, 1H), 1.84-1.73 (m, 4H), 1.25-1.23 (m, 32H), 0.88-0.82 (m, 6H). Calcd for C₄₁H₅₅NO (577.90): C, 85.21; H, 9.59; N, 2.42. Found: C, 84.62; H, 9.41; N, 2.29.

Poly[4-(1-decylundecyl)-4H-benzo[def]carbazole-1,7-ylene] (**1,7-PBCza**). Similarly polymerization of **7a** gave **1,7-PBCza** as a green solid (0.15g, 72%). ¹H NMR (400 MHz, CDCl₃) δ [ppm]: 8.07 (s, 4H), 7.68 (s, 2H), 4.76(m, 1H), 2.47 (m, 2H), 2.10 (m, 2H), 1.30-1.16 (m, 32H), 0.80-0.77 (m, 6H). Calcd for C₃₅H₅₁N (485.80): C, 86.53; H, 10.28; N, 2.88. Found: C, 85.95; H, 10.35; N, 2.92.

2.2 General method and instrumentation

All synthetic manipulations were performed by a standard technique using a Schlenk tube under an argon atmosphere. Column chromatography was performed using a silica gel (Kanto Chem., 60 N, 63-120 mm). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECS 400 spectrometer. The ¹H and ¹³C chemical shifts are given in units of δ (ppm) relative to δ (TMS) = 0.00 and δ(CDCl₃) = 77.0 ppm, respectively. Photoabsorption in the range of ultraviolet-visible (UV-vis) and photoluminescence (PL) measurements of the polymer samples in CHCl₃ and in a form of a thin film coating on a quartz glass were performed using a Shimadzu UV-1800 spectrophotometer and an F-4500 fluorescence spectrophotometer (Hitachi) at room temperature. The fluorescence quantum yield (φ_{fl}) in CHCl₃ were relative to 9,10-diphenylanthracene in cyclohexane (φ_{fl} = 0.90) as a standard. The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the polymers were estimated by a gel permeation chromatography (GPC) system (Shimadzu, LC solution) using polystyrene standards with CHCl₃ as an eluent. Cyclic voltammetry (CV) of polymers in thin film on a Pt disk was performed at a scan rate of 50 mV/s in acetonitrile containing 0.1 M Et₄NBF₄ at room temperature under Ar using a saturated calomel electrode (SCE) as the reference and platinum wire as the counter electrode. The electrochemical data (vs SCE) obtained by cyclic voltammetry was made a correction with the redox potential (4.8 eV) of ferrocene/ferricinium [20, 21]. Elemental analyses were carried out with

a Perkin-Elmer type 2400 apparatus. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out by an Extar 7000 TG/DTA (Seiko) analyzer at a heating rate of 10 °C min⁻¹ in an argon atmosphere.

3. Results and discussion

3.1 Synthesis

The general synthetic routes toward the monomers and polymers are outlined in Scheme 2 and Scheme 3. The introduction of the 1-decylundecyl group at N-position of **3** was carried out by the procedure reported previously [22], giving **4a**. The *p*-(1-decylundecyloxy)phenyl group was introduced into N-position of **3** according to the procedure in our previous report [23], giving **4b**. Monomers **5a** and **5b** were prepared by oxidation of **4a** and **4b** with DDQ, respectively. In order to obtain **7a**, debromination of **5a** and successive bromination of **6a** were performed. Homopolymerizations of **4a**, **4b**, **5a**, **5b** and **7a** by Yamamoto reaction [24] afforded **PECza**, **PECzb**, **PBCza**, **PBCzb** and **1,7-PBCza**, respectively.

All of the polymers were soluble in usual organic solvents such as toluene, THF, CHCl₃, and so forth. GPC results were summarized in Table 1. They have good processability to make thin cast films. The polymers showed M_n larger than 10 kg mol⁻¹, the polydispersities (M_w/M_n) about 1.5, and the degree of polymerization (DP) higher than 27. TGA results are shown in Fig. 2. All the polymers showed a good thermal stability, and their temperatures of 5 wt % loss in TGA (T_d) were around 400 °C, respectively. The polymers with N-phenyl side group showed lower T_d values. This result suggests that thermal stability of **PECzb** and **PBCzb** are lower than those of N-alkyl substituted polymers (**PECza**, **PBCza**, and **1,7-PBCza**), which might be due to suppression of intimate interaction between polymer chains by steric effect of the rigid N-phenyl group.

Table 1

GPC and TGA results of the polymers.

Polymer	M_n (kg mol ⁻¹)	M_w (kg mol ⁻¹)	M_w/M_n	DP ^a	T_d (°C) ^b
PECza	78.3	107.7	1.38	161.4	464
PECzb	121.1	229.7	1.89	209.8	377
PBCza	13.3	18.9	1.42	27.6	422
PBCzb	299.2	528.2	1.76	520.3	366
1,7-PBCza	13.0	19.9	1.57	27.0	436

^aDP was estimated from M_n .

^bTemperature of 5 % weight loss determined by TGA under an argon atmosphere.

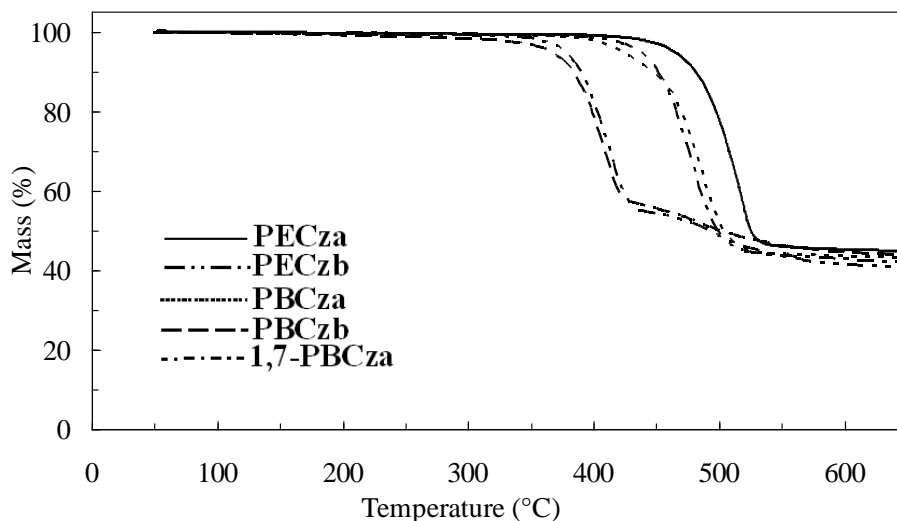


Fig. 2 TGA curves of the polymers.

3.2 Optical properties.

The photophysical properties of dilute solution and thin films of all the polymers were investigated by UV-vis and PL, and the results are shown in Fig. 3 and Fig. 4. The UV-vis and PL spectra data for the polymer are summarized in Table 2.

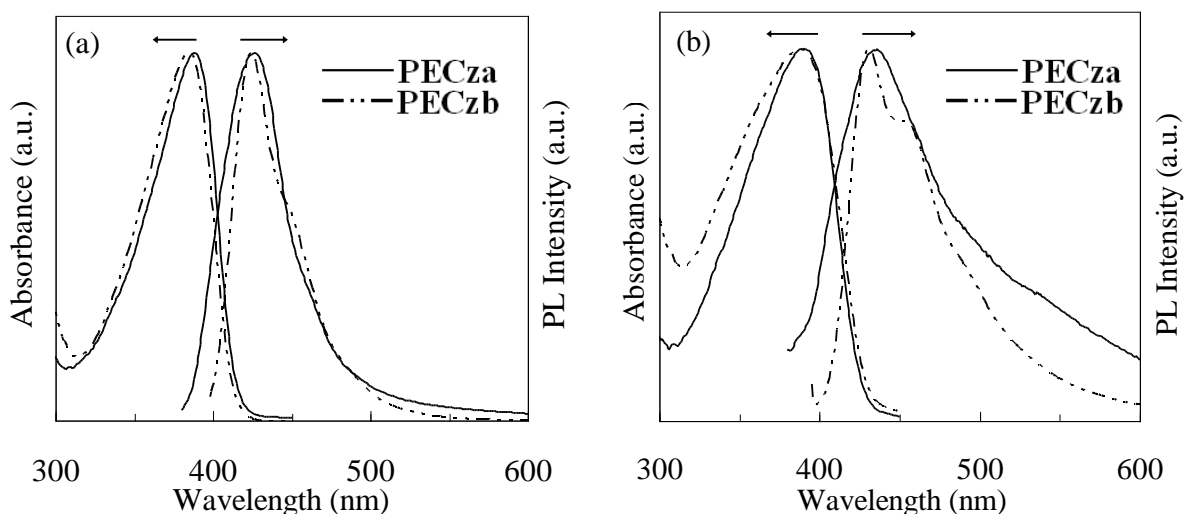


Fig. 3 UV-vis and PL spectra of **PECza** and **PECzb** in CHCl_3 (a) and flim state (b).

Fig. 3a shows the absorption and PL spectra of **PECza** and **PECzb** in CHCl_3 . The absorption feature with a pronounced π - π^* transition peak around 385 nm observed for **PECza** was almost the same as that of **PECzb**. The absorption maxima ($\lambda_{\text{max, Abs}}$) of the series of **PECz** were similar with those of poly(2,7-carbazole)s (**PCz**) ($\lambda_{\text{max, Abs}} = 387 \text{ nm}$) [25, 26]. The PL emission peak maxima ($\lambda_{\text{max, Em}}$) of the polymers in CHCl_3 were observed at 426 nm for **PECza** and 424 nm for **PECzb**. The fluorescence quantum yields (ϕ_f) of **PECza** and **PECzb** in CHCl_3 ($\phi_f = 0.45, 0.67$) were lower than those of **PCz** ($\phi_f \approx 1$). The Stokes shifts ($\Delta\lambda = (\lambda_{\text{max, Em}}) - (\lambda_{\text{max, Abs}})$) of **PECza** and **PECzb** in

CHCl₃ were 38 and 39 nm, respectively, which were slightly larger than those of **PCz** (ca. 35 nm) [26]. The larger $\Delta\lambda$ is responsible for the larger structural change between ground and excited states, which might affect lowering ϕ_1 .

The absorption and PL spectra of **PECza** and **PECzb** in the thin film state are shown in Fig. 3b. Their absorption spectra were almost the same each other, and the energy gaps (E_g) between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the **PECza** and **PECzb** estimated from the onset of the absorption spectra in the film state were 2.94 and 2.96 eV, respectively, which were almost the same with those of **PCz** (2.92 eV).

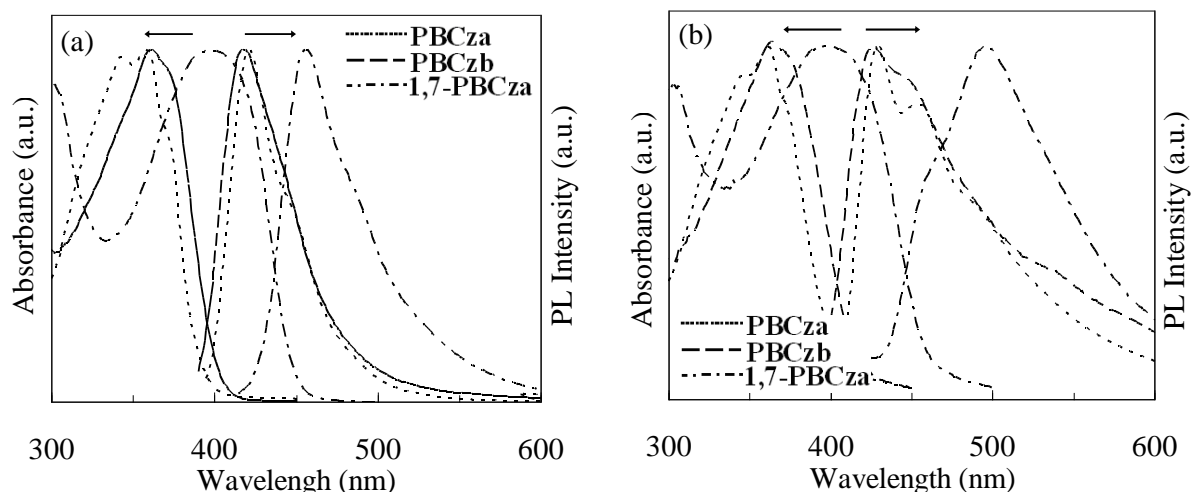


Fig. 4 UV-vis and PL spectra of **PBCza**, **PBCzb** and **1,7-PBCza** in CHCl₃ (a) and film state (b).

Next, absorption and PL spectra of **PBCz** in CHCl₃ are depicted in Fig. 4a. The observed $\lambda_{\max, \text{Abs}}$ at 358 nm for **PBCza** and 361 nm for **PBCzb** owing to π - π^* transition of conjugated polymer main chains were unexpectedly blue-shifted in comparison to **PCz** and poly(2,7-phenanthrene)s [27, 28], although they include an extended π -conjugated structure of phenanthrene in the unit. Consequently, they fluoresced in deep-blue color in CHCl₃, and the $\lambda_{\max, \text{Em}}$ of **PBCza** and **PBCzb** were observed at 421 nm and 419 nm, respectively. The $\Delta\lambda$ observed for **PBCza** and **PBCzb** in CHCl₃ were 63 and 58 nm, which were larger than those of **PECz** and **PCz** (35-39 nm). The larger $\Delta\lambda$ of **PBCza** and **PBCzb** might be responsible for the lower ϕ_1 than those of **PECz** and **PCz**. These results suggest that the 4,5-ethynylene bridge and the N-bridge cooperatively control each ring strain and 2,7-conjugation of polycarbazole and polyphenanthrene i.e., an optimized structure of **BCz** calculated by DFT showed both features of an elongated C-N linked **Cz** and a strained phenanthrene with the imino bridge (Fig. 1S, Table 1S and Table 2S, Supporting information).

Fig. 4b shows the absorption and PL spectra of **PBCza** and **PBCzb** in the thin film state. Due to some aggregations or interactions between the polymer chains in the thin film state, the $\lambda_{\max, \text{Abs}}$ of **PBCza** and **PBCzb** were slightly red-shifted than those in CHCl₃. The E_g of **PBCza** (3.15 eV) and **PBCzb** (3.05 eV) were larger than those of **PECz** and **PCz**. The large E_g values of **PBCz** were responsible for the blue shifts of $\lambda_{\max, \text{Abs}}$ in solution. The PL spectra of **PBCz** in the film state showed tailing bands that might involve vibronic feature and excimeric emissions in the longer wavelength region.

The absorption and PL spectra of **1,7-PBCza** in CHCl₃ are also shown in Fig. 4a. The $\lambda_{\max, \text{Abs}}$

was observed at 396 nm, which was considerably red-shifted in comparison with those of poly(3,6-carbazole)s ($\lambda_{\text{max, Abs}} = \text{ca. } 310 \text{ nm}$) [29,30]. The large red-shift is due to effect of the added 4,5-ethynylene bridge at the **Cz** ring with extension of π -conjugation along the main chain through the 1,7-linkage and the bridge. The $\lambda_{\text{max, Em}}$ was observed at 456 nm, and the $\Delta\lambda$ was 60 nm. Interestingly, the ϕ_{fl} (=0.45) was surprisingly high compared with those ($\phi_{\text{fl}} = 0.04$ to 0.06) for poly(3,6-carbazole)s in dichloromethane [30]. The enhancement of quantum yields might be due to stabilization of energy states of **1,7-PBCza** by the extended π -conjugation. Fig. 4b shows the absorption and PL spectra of **1,7-PBCza** in the thin film state. The $\lambda_{\text{max, Abs}}$ of **1,7-PBCza** was largely red-shifted compared with those of **PECz**, **PBCz**, and **PCz**. The E_g of **1,7-PBCza** is exceptionally narrow compared with those of poly(3,6-carbazole)s (3.2 eV) [30]. The emission band of **1,7-PBCza** was much broader and shifted to lower energy compared with that ($\lambda_{\text{max, Em}} = 426 \text{ nm}$) of poly(3,6-carbazole)s [30]. These photophysical results suggest that **1,7-PBCza** is a potential polymer having light-emitting as well as hole transporting functions to be applied in PLEDs.

Table 2

Optical properties, HOMO-LUMO energy gaps, and the energy levels of the polymers.

Polymer	$\lambda_{\text{max, Abs}}$ (nm)		$\lambda_{\text{max, Em}}$ (nm)		$\Delta\lambda^a$ (nm)	ϕ_{fl}	E_g (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)
	in CHCl_3	film	in CHCl_3	film					
PECza	388	388	426	436	38	0.45	2.96	−5.59	−2.54
PECzb	385	389	424	431	39	0.67	2.94	−5.53	−2.59
PBCza	358	361	421	429	63	0.30	3.15	−5.50	−2.44
PBCzb	361	361	419	426	58	0.48	3.05	−5.49	−2.44
1,7-PBCza	396	398	456	495	60	0.45	2.77	−5.37	−2.60

^aStokes shifts measured in CHCl_3 .

3.3 Electrochemical properties

Electrochemical data of the polymers were measured by cyclic voltammetry (CV) and their voltammograms are shown in Fig. 5 and related data are summarized in Table 2. The energy levels of HOMO (E_{HOMO}) estimated from the onset potential of an oxidation peak of **PECza** and **PECzb** were −5.59 and −5.53 eV, respectively, which were similar to those of **PCz** (ca. −5.6 eV) [26]. The E_{HOMO} of **PBCza** (−5.50 eV) and **PBCzb** (−5.49 eV) were shallower than those of **PECz**. The shallowest E_{HOMO} (−5.37 eV) was observed for **1,7-PBCza**, although it was deeper than those of the comparison poly(3,6-carbazole)s (ca. −5.10 eV) [30].

Since it was difficult to recognize onset potentials of reduction waves of the homopolymers in the film state, the energy levels of the LUMO (E_{LUMO}) were estimated from the E_{HOMO} and optical band gap (E_g) using the equation, $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g$. The E_{LUMO} of **PECza**, **PECzb**, **PBCza**, **PBCzb** and **1,7-PBCza** were determined to be −2.54, −2.59, −2.44, −2.44 and −2.60 eV, respectively.

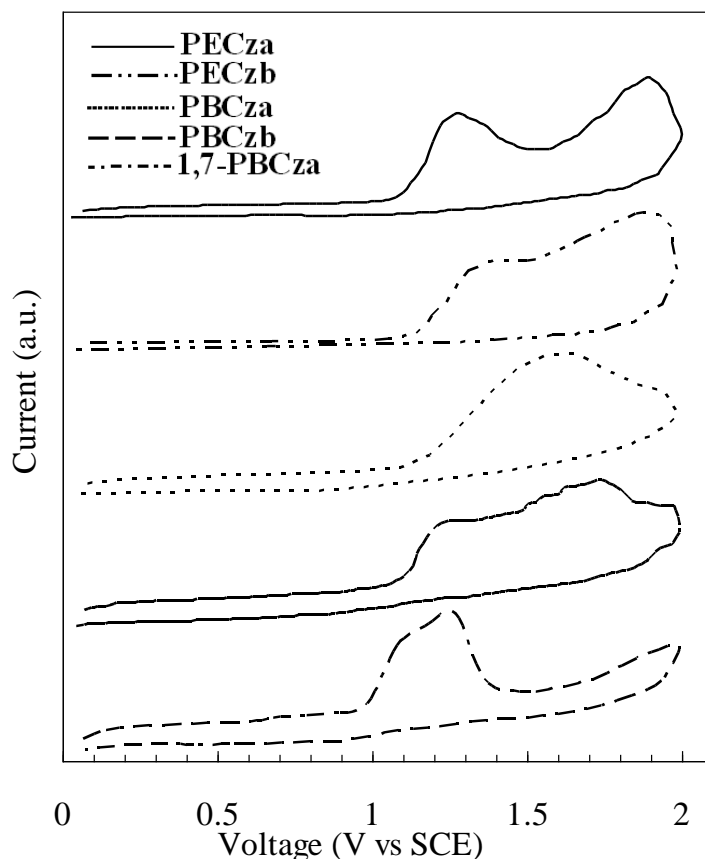


Fig. 5. Cyclic voltammograms of **PECza**, **PECzb**, **PBCza**, **PBCzb** and **1,7-PBCza**.

To understand the difference of E_{HOMO} between **PCz** and **PBCz**, the electronic structures of **Cz** and **BCz** were investigated using density functional theory (DFT) in the Gaussian 09 program at the B3LYP/6-31G(d) basis set. Fig. 6 shows the optimized geometry and electron density distributions in the HOMO and LUMO for the different building blocks. It appears that the electron delocalized along the whole rings well on both the HOMO and LUMO of **Cz** and **BCz**, therefore scope of delocalization in the **BCz** is wider for the larger fused aromatic ring system. As a result, E_{HOMO} of **BCz** is elevated and E_g narrowed compared to those of **Cz** by the calculation. This calculation also indicates that the **BCz** unit can function as phenanthrene by presence of the 4,5-ethenylene bridge of **Cz**.

Considering the electron density maps of HOMO of the **Cz** and **BCz** units, conjugation along the main chain through 2,7-linked **PCz** is thought to be more advantageous than 2,6-linked **PBCz**, because no electron density could be observed in the center of the **BCz** unit. Thus, the wider E_g observed for **PBCz** can be accounted for the characteristic electron distribution of **BCz**. Similarly, the narrow E_g of **1,7-PBCza** can be elucidated by π -conjugation of 1,7-linkage through 8,9-ethenylene of **BCz**.

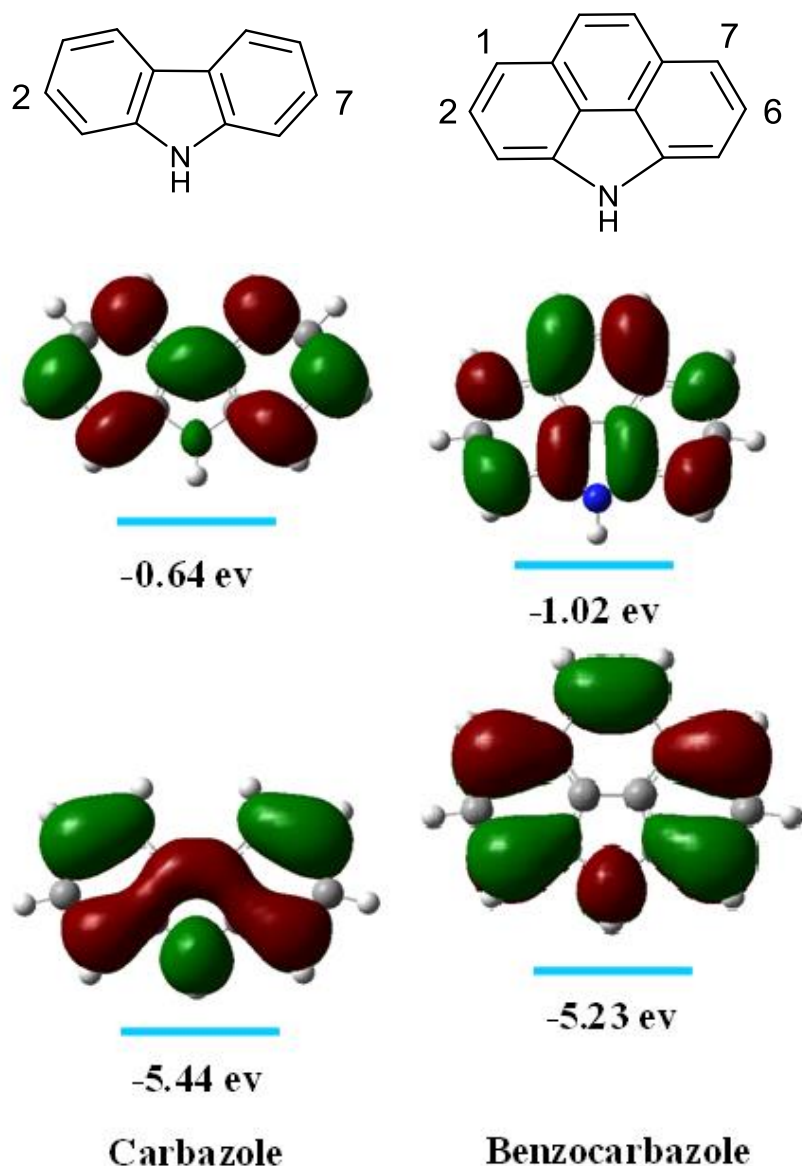


Fig. 6 HOMO and LUMO energy levels of carbazole (**Cz**) and benzocarbazole (**BCz**), optimized by DFT calculation with Gaussian 09 program at the B3LYP/6-31G(d) basis set.

3.4 X-ray diffraction analysis

The X-ray diffraction (XRD) analyses were performed to investigate π -stacking distance and structural order of the polymers in film state, and the results are shown in Fig. 7. **PECza** and **PECzb** had a broad diffraction hump observed at about 18-19° ($d = 4.8, 4.7 \text{ \AA}$). On the other hand, **PBCza**, **PBCzb** and **1,7-PBCza** exhibited diffraction humps in the wider angle at $2\theta = 20.50, 21.32, 21.10^\circ$, which correspond to π -stacking distances of 4.33, 4.16, 4.21 \AA , respectively. Since all the polymers had no sharp diffraction peaks but only broad humps, these polymers are considered to be amorphous with loose π -stacking. The smaller π -stacking distances observed for **PBCz** suggests that the intermolecular interaction is stronger compared with **PECz**, which is basically affected by the size of the conjugated planar unit of the polymers.

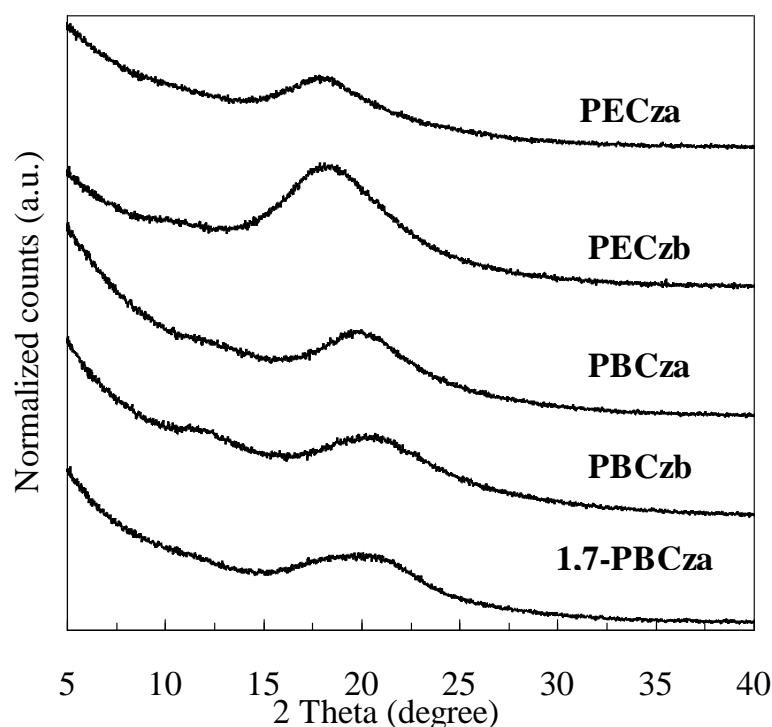


Fig. 7 X-ray diffraction patterns of the homopolymers.

4. Conclusions

In this article, we have presented the syntheses and characterizations of 4,5-ethylene bridged poly(carbazole)s (**PECza**, **PECzb**) and poly(4*H*-benzo[*def*]carbazole)s (**PBCza**, **PBCzb** and **1,7-PBCza**) as a new series of carbazole-based homopolymers. They had enough high molecular weights, good solubility in common organic solvents, good thermal stability for making thin films and amorphous nature in the film state. **PECz** showed similar electronic properties of absorption and emission to those of **PCz**, but the ϕ_{H} were somewhat lower than those of **PCz**. On the other hand, poly(2,6-benzocarbazole)s (**PBCza** and **PBCzb**) showed unexpectedly blue-shifted absorption bands, the shallower E_{HOMO} , and the wider E_{g} compared with those of **PECz** and **PCz**, although they have the larger π -conjugation in the monomer unit. These results might be ascribed to the dominant characteristics of poly(2,7-phenanthrene) strained by the N-bridge in **PBCz**.

The PL emission colors can be evaluated by color coordinates in the Commission Internationale de L'Eclairage (CIE) chromaticity diagram. The CIE(*x*, *y*) values of **PECza**, **PECzb**, **PBCza** and **PBCzb** in CHCl_3 were almost identical to (0.15, 0.05) in the region of deep blue. In film state, the CIE values for **PECz** (0.16, 0.15) were in the region of blue, while PL emission color of **PBCz** were shifted to greenish blue but kept in the region of blue (0.19, 0.21). The shift of the PL color is ascribed to the stronger intermolecular interaction between the larger planar units of **PBCz** as suggested in the XRD results, although they have larger E_{g} than **PECz**. From the appropriate E_{HOMO} around -5.5 eV for hole injection and appropriate E_{g} for blue emission, it is considered that **PECz** and **PBCz** have potential to be applied in PLED as the blue-light emitting material. On the other hand, **1,7-PBCz** is found to have unique properties, i.e., the absorption and emission bands were observed in considerable longer region in wavelength with moderate ϕ_{H} , which were quite different from those of poly(3,6-carbazole)s. According to the dominant character of poly(1,8-phenanthrene) trained by the 8,9-ethenylene bridge in **1,7-PBCza**, it showed the shallowest E_{HOMO} and narrowest

E_g of all the homopolymers synthesized in this work. Consequently, it fluoresced in blue green (CIE (0.20, 0.33)) in the film state. Therefore, the **1,7-BCz** unit would rather be applied in a donor component of donor-acceptor-type narrow band gap polymers for organic solar cells.

Appendix A. Supplementary data

Additional Supporting Information about synthetic procedures, characterizations of other materials, optimized geometric structures, bond angles and bond lengths.

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Highlights

- New poly(carbazole)s having 4,5-ethenylene and ethylene bridges were synthesized.
- The polymers had appropriate M_n , solubility, and ϕ_1 to be applied in emissive devices.
- Poly(2,6-benzocarbazole)s had appropriate band gap for blue-light emitting.
- Poly(1,7-benzocarbazole) had narrower band gap than the 2,6-linked ones.

Graphical Abstract

